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Supporting information

Fabrication and Electrochemical Properties of Three Dimensional (3D) Porous Graphitic and Graphene-like Electrodes Obtained by Low-Cost Direct Laser Writing Methods

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Optical microscopy

Figure S1 shows detailed optical microscopy images of LIG electrodes written at laser burn times between 10 and 120 ms/pix. Images captured at 10 ms/pix interval show progressive better definition and connection between individual pixels as well as progressive thickening from nominal 100 μm at 10 ms/pix to 130 μm at 120 ms/pix.

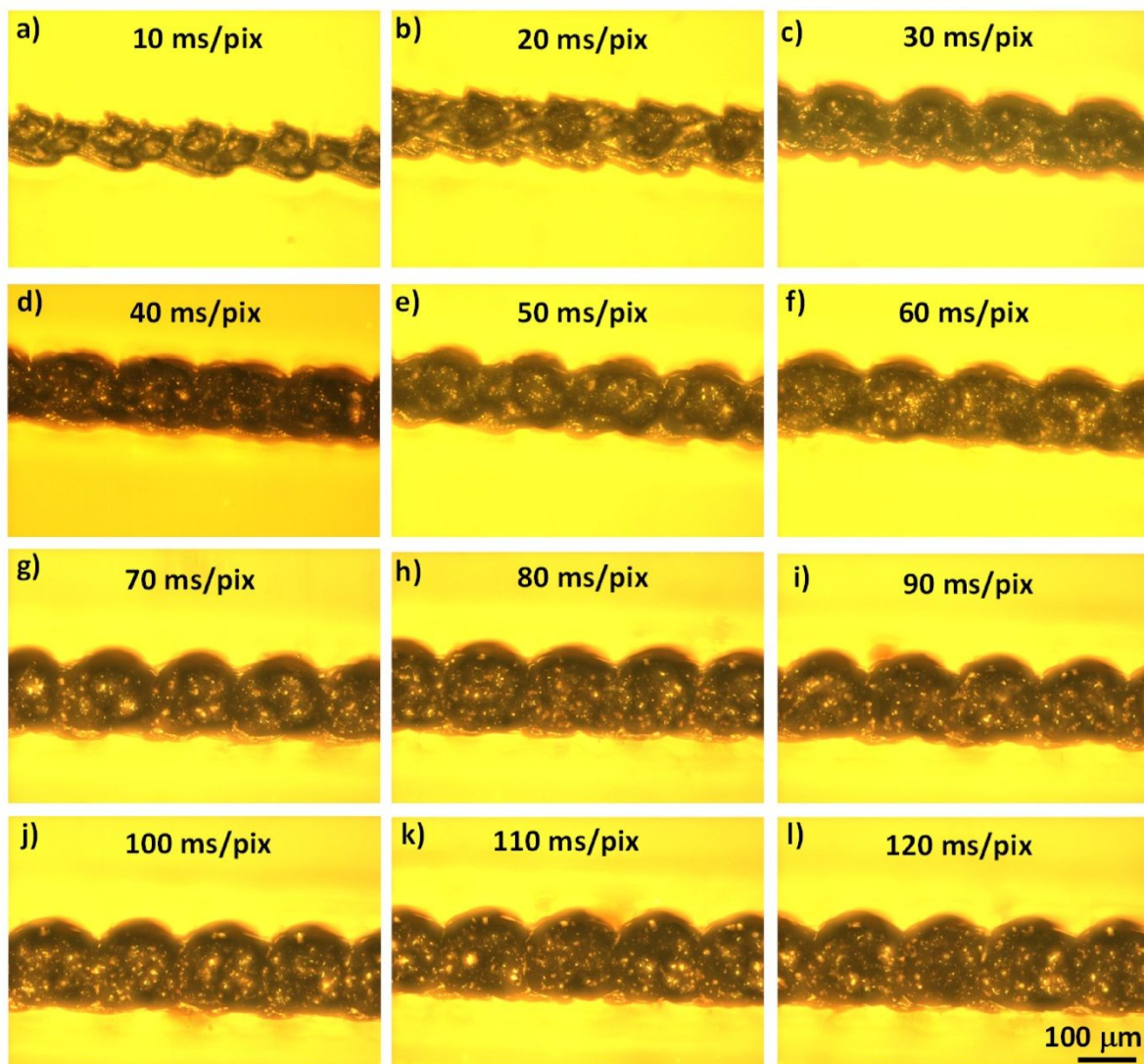


Figure S1. Optical microscopy images (a – l) of LIG electrodes written at laser burn times 10 - 120 ms/pix.

Scanning electron microscopy

SEM images in Figure S2 show progressive thickening of formed electrodes and increased pore sizes with the increase of the laser burn time from 10 to 120 ms/pix.

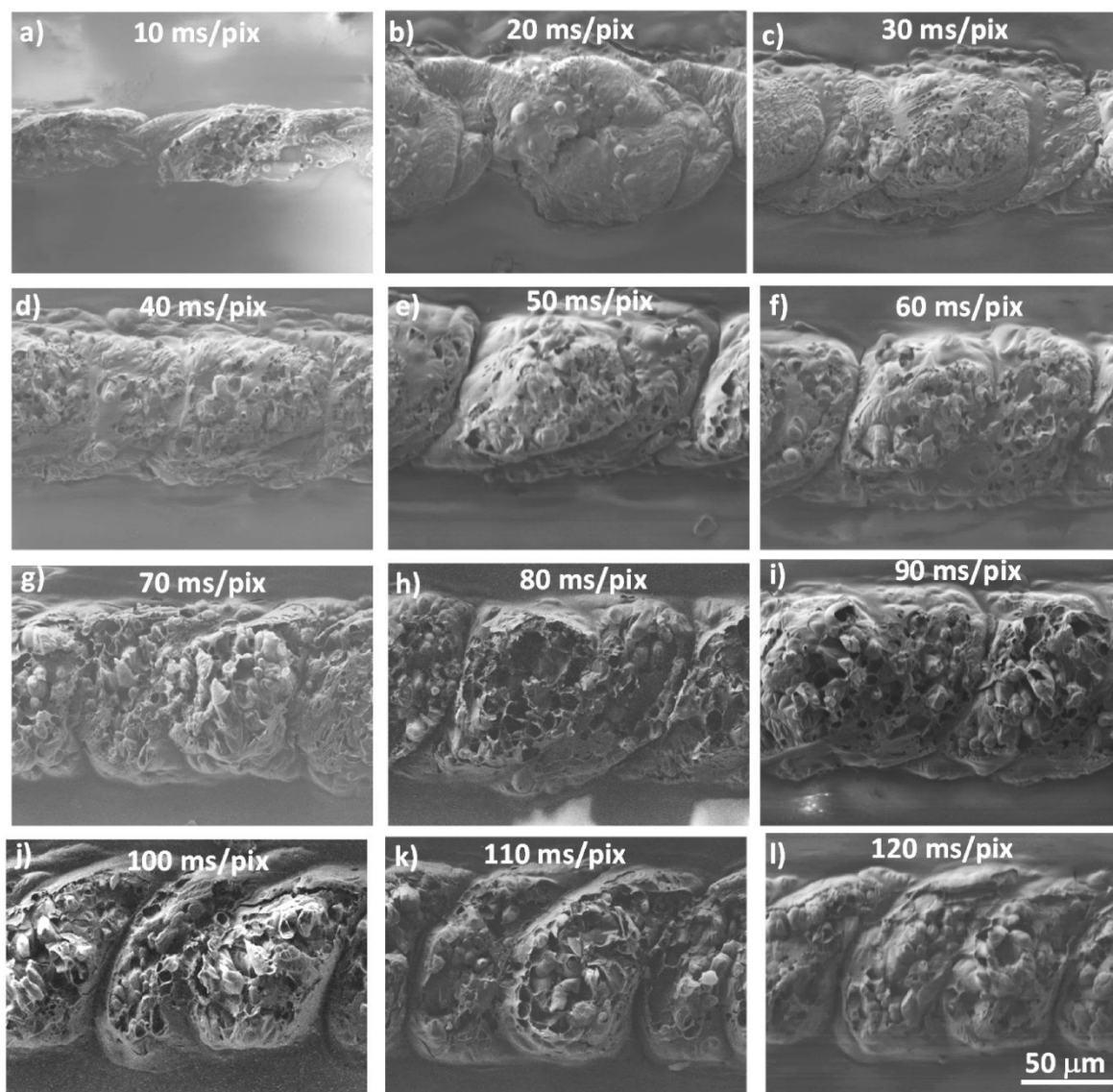


Figure S2. SEM images (a-l) of LIG electrodes written at laser burn times 10 -120 ms/pix.

Determination of specific surface area

The α_s plot method was used for the determination of surface area. Adsorption / desorption isotherm was measured for nitrogen (N_2) using 22.6 mg of carbon scraped off from LIG structures obtained at 50 ms/pix. The results of the isotherms are shown in Fig. S3b. V_a represents the total gas volume adsorbed whereas p / p_0 is the pressure ratio. The shape of the adsorption isotherm is of type I, which corresponds to microporous materials. The sharp increase of the adsorbed volume, V_a , for the low p / p_0 values is due to the filling of micropores of molecular dimensions (< 1 nm). At the higher p / p_0 values, the rise of V_a values might be due to the macro-porous nature of the carbon sample. For the sample analyzed, the surface area was calculated to be $428 \text{ m}^2 \text{ g}^{-1}$.

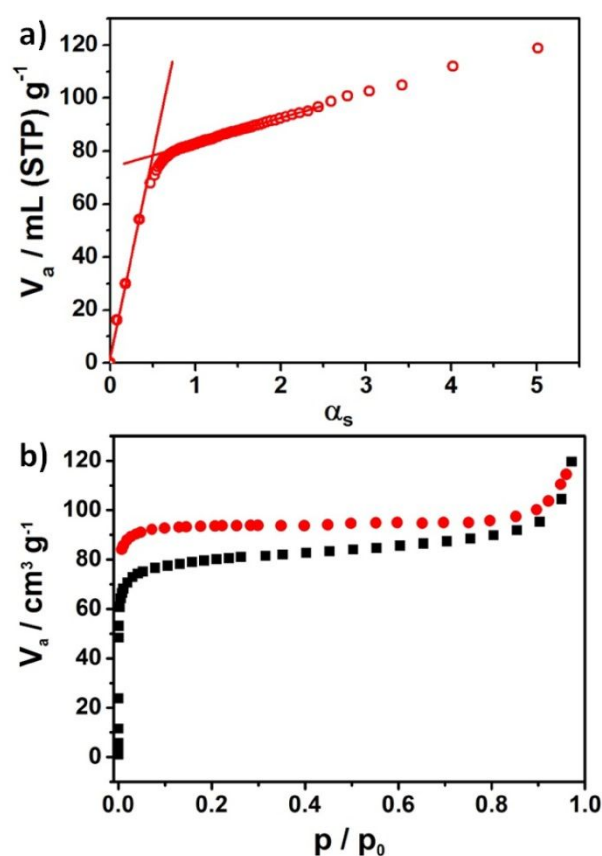


Figure S3. a) α_s plot for the determination of the surface area; b) Adsorption (black squares) / desorption (red circles) isotherm obtained for 50 ms/pix LIG material.

Contact angle measurements

Figure S4 shows details of LIG surface properties by contact angle measurements. The LIG surface showed hydrophobicity comparable to pristine kapton tape at 20 and 50 ms/pix burn times. Higher hydrophobicity was calculated for higher burn times. The calculated contact angles (θ_c) are the following: Kapton = 91° , LIG 20 ms/pix = 85° ; LIG 50 ms/pix = 94° ; LIG 80 ms/pix = 146° ; LIG 110 ms/pix = 128° .

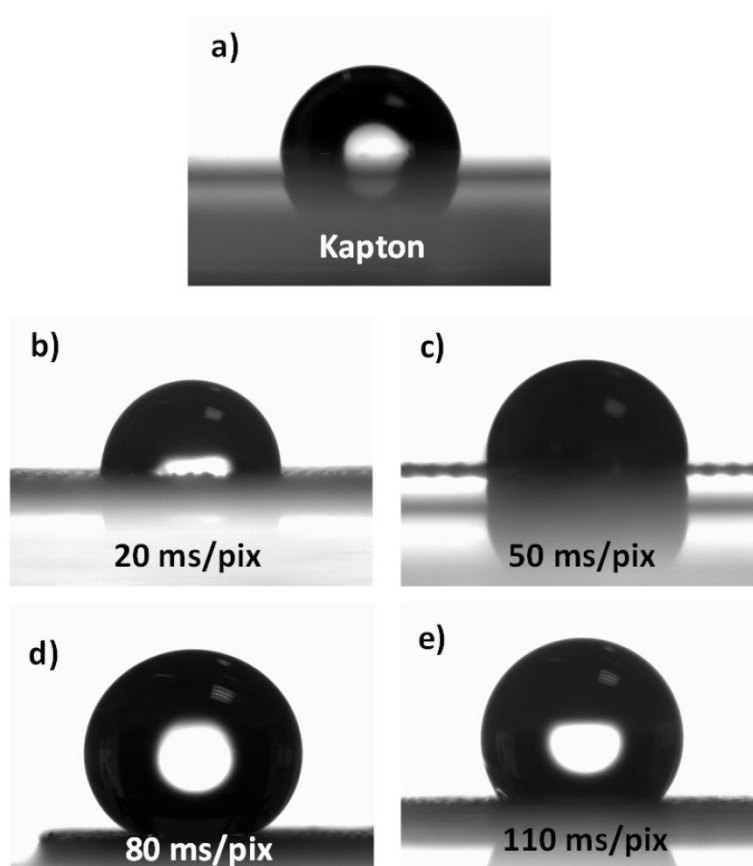


Figure S4. Characterization of surface property by contact angle for a) kapton tape; b) LIG 20 ms/pix; c) LIG 50 ms/pix; d) LIG 80 ms/pix; e) LIG 110 ms/pix.

Raman analysis details

Figure S4 report spectral variations in D, G, 2D peak positions measured over 23 collected spectra in the 10 – 110 ms/pix burn time range. Full width-at-half-max (FWHM) measured in the 10 – 110 ms/pix burn time range for 2D peak as well as I_{2D}/I_G is also reported across burn times.

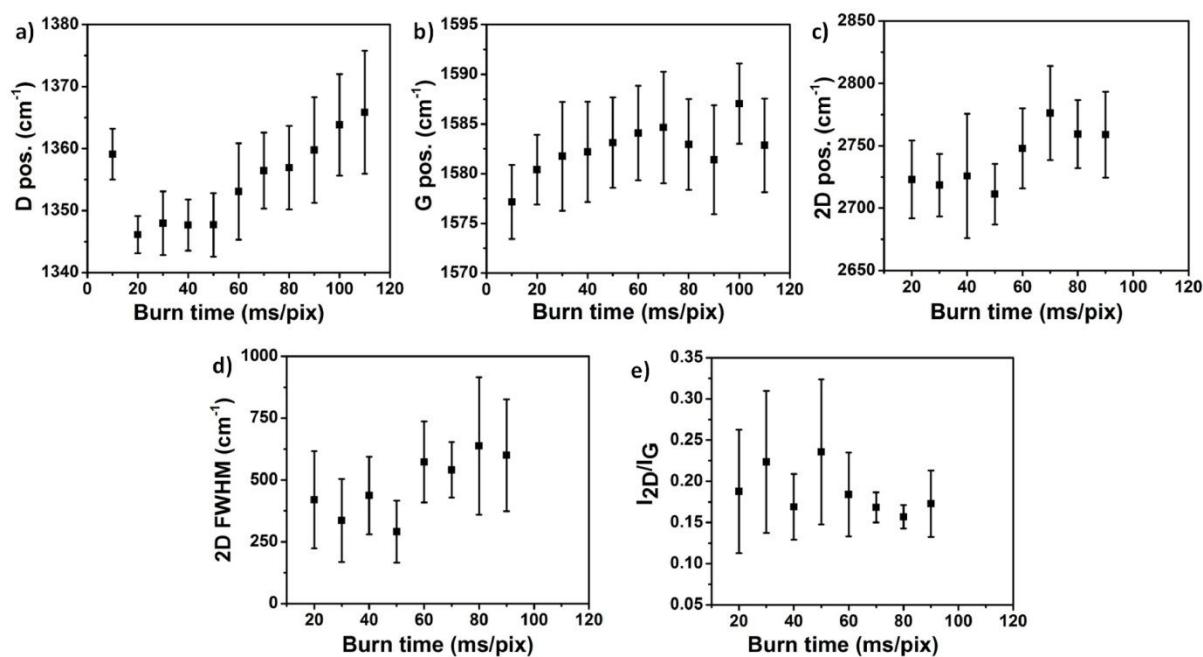


Figure S5. Variation of D,G and 2D peak position (a-c), 2D FWHM (d) and I_{2D}/I_G (e) trend measured from Raman spectra collected for LIG electrodes written in the interval 10 -120 ms/pix.

XPS Analysis

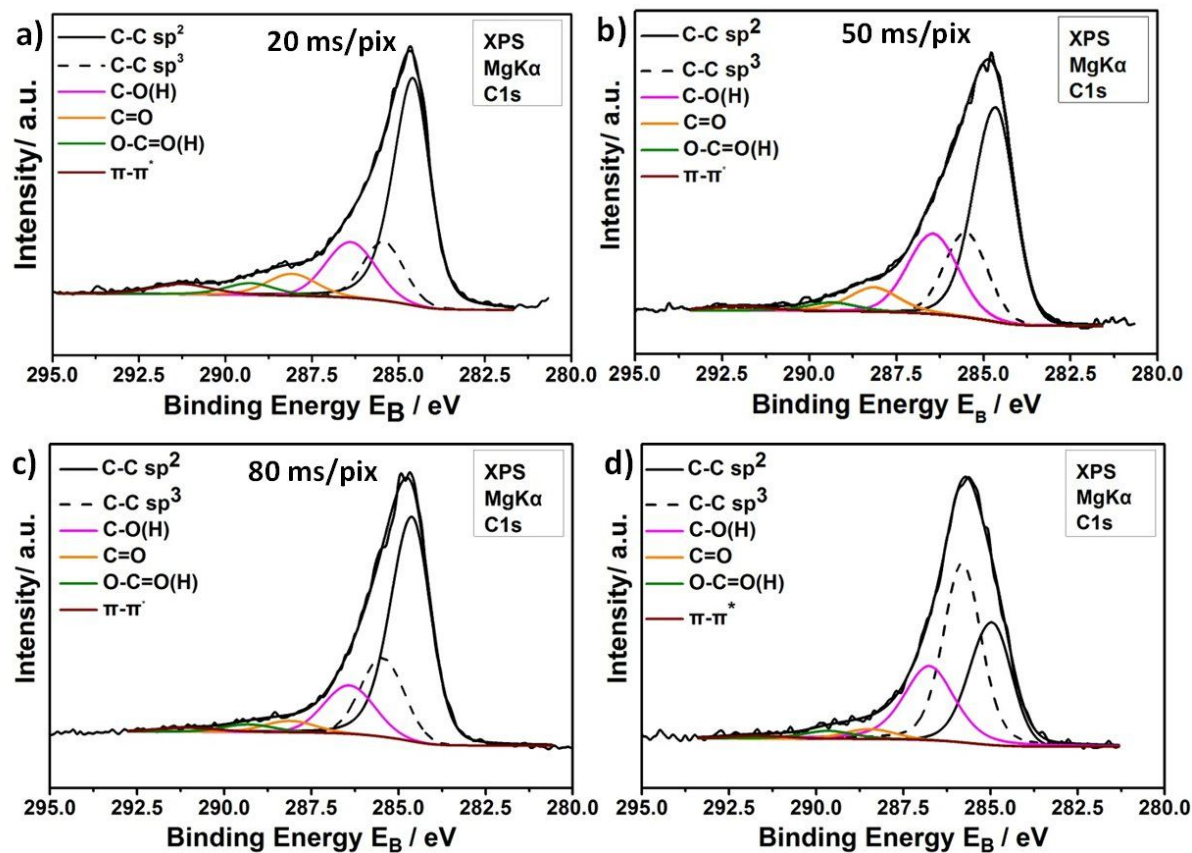


Figure S6. Deconvoluted C1s XPS peak of LIG electrodes fabricated at a) 20, b) 50, c) 80 and d) 110 ms/pix laser burn times.

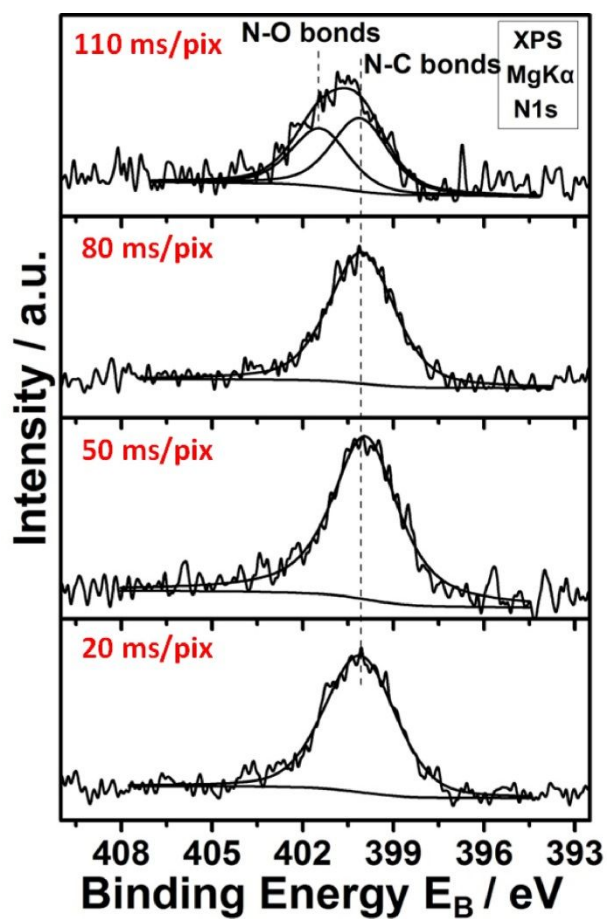


Figure S7. Deconvoluted N1s XPS peak of LIG electrodes fabricated at 20, 50, 80 and 110 ms/pix laser burn times.

Electrochemical setup

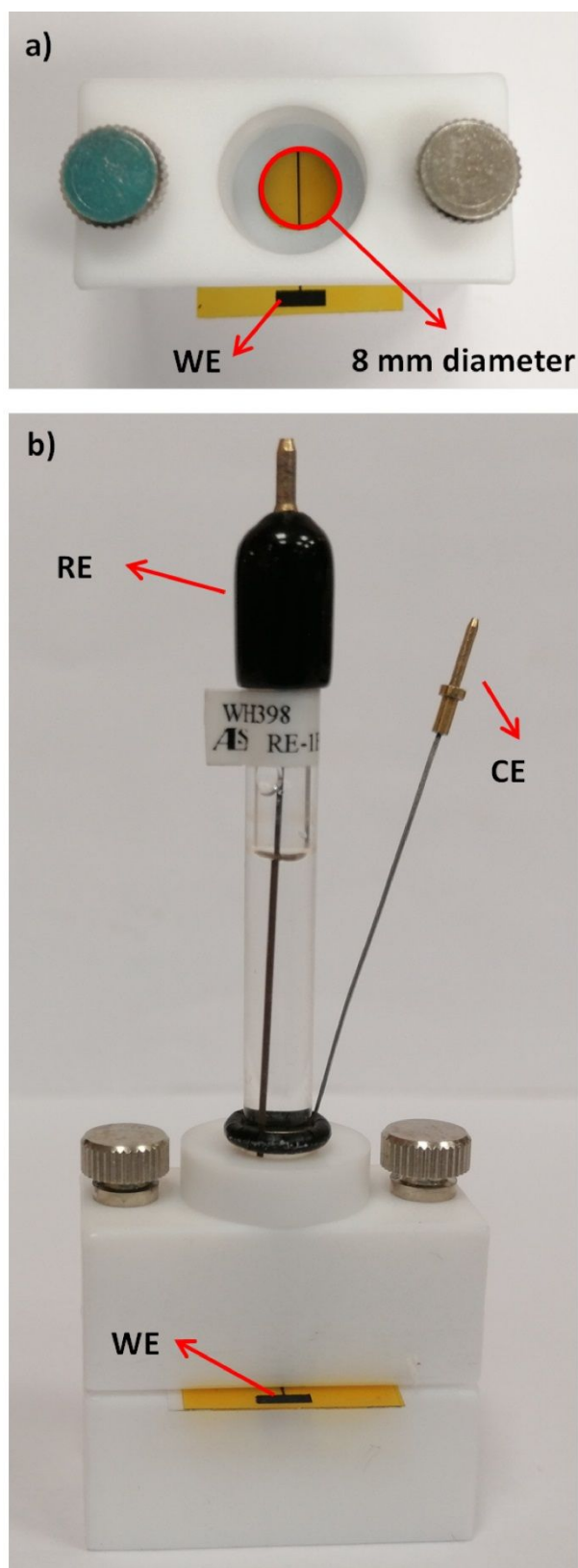


Figure S8. Photographs of a) one electrode electrochemical platform assembled in a Teflon electrochemical cell; b) complete electrochemical cell showing LIG working electrode (WE),

Ag/AgCl reference electrode (RE) and Pt wire working electrode (WE). Free domain photographs courtesy of author Eoghan Vaughan.

Cyclic Voltammetry

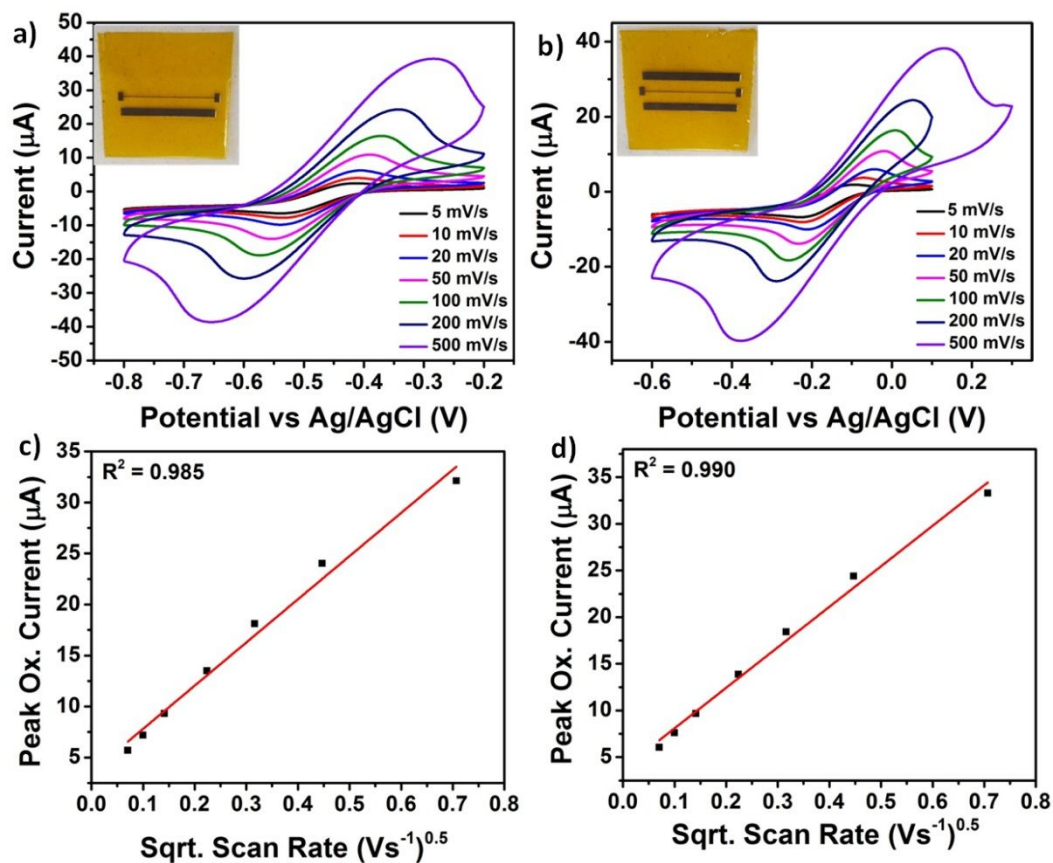


Figure S9. Cyclic voltammograms of 50 ms/pix LIG electrodes for 5 mM $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ in 0.1 M KCl solution as supporting electrolyte recorded with a) LIG working and counter electrode and Pt wire as reference electrode; b) all carbon system. Insets: photographs of the LIG electrodes; c -d) Peak oxidation current vs square root of scan rate for a-b).

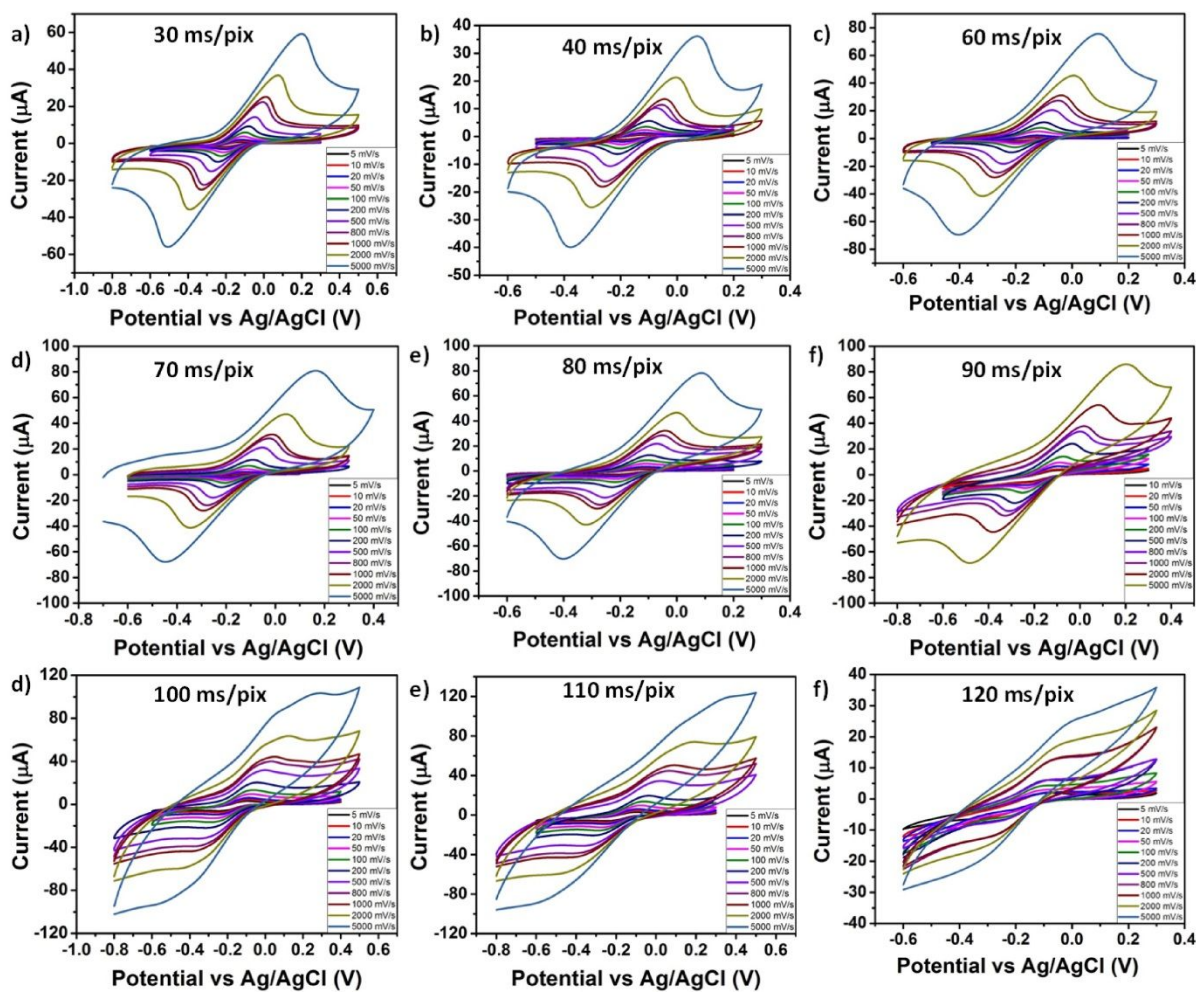


Figure S10. Cyclic voltammograms of LIG electrodes written between 30 and 120 ms/pix burn times (a-f) for 5 mM $\text{Ru}(\text{NH}_3)_6^{3+/2+}$ in 0.1 M KCl solution as supporting electrolyte.

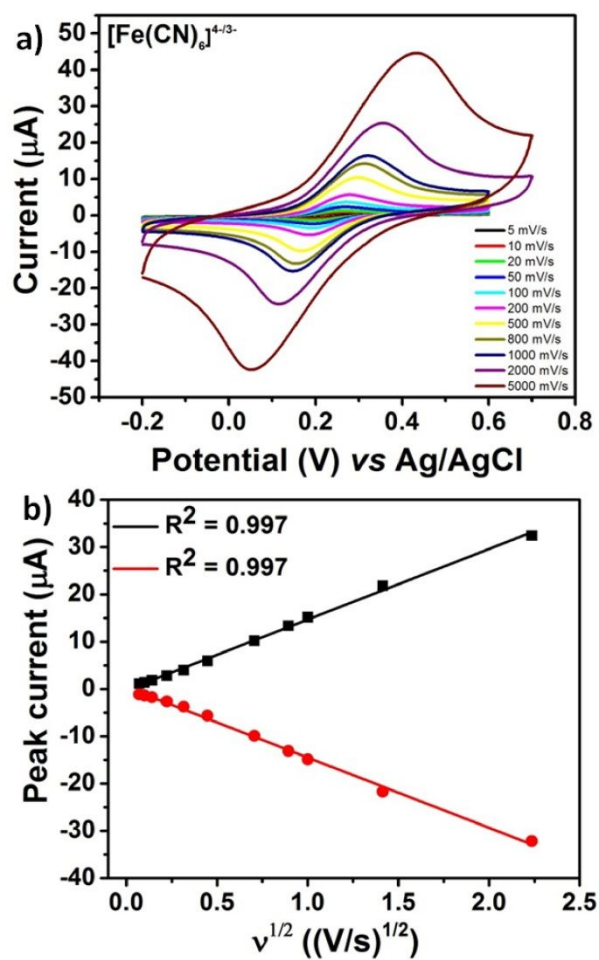


Figure S11. a) Cyclic voltammograms of LIG electrode 50 ms/pix at different scan rates in 5 mM $\text{Fe}(\text{CN})_6^{3-/4-}$ / 0.1 M KCl; b) Current peak n values vs square root of potential scan rate.